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Fabrication and Evaluation of Polyvinylidene Flouride/Polyvinyl Alcohol (PVA/PVDF) Hybrid Membranes for Lithium-Air Battery Applications

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FABRICATION AND EVALUATION OF POLYVINYLIDENE FLOURIDE/POLYVINYL ALCOHOL (PVA/PVDF) HYBRID MEMBRANES FOR LITHIUM-AIR BATTERY APPLICATIONS

By

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I dedicate this work to my late Father, Engr. O. E. Akpanekong
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A new type of hybrid hydrophobic/hydrophilic membrane is proposed in this thesis to improve the electrochemical performance of Lithium-Air battery operated with dual electrolytes. The dual electrolytes include an organic and aqueous electrolyte which is separated from one another by this solid-state hybrid polymer membrane so that they do not intermix. Also, this solid-state hybrid polymer membrane is conductive to facilitate the ionic charge carriers transport between the dual electrolytes. With polyvinylidene fluoride (PVDF) used as a hydrophobic polymer while polyvinyl alcohol (PVA) used as the hydrophilic polymer, the hybrid membranes were prepared by phase inversion and polymer solution casting processes to test the novel concept being proposed in this study. Moreover, the ionic conductivity, electrochemical stability, permeability, and morphology of the prepared PVDF/PVA hybrid membranes have been investigated to examine their suitability for Lithium-Air battery applications. The experimental results suggest that the PVDF/PVA hydrophobic/hydrophilic hybrid membrane is stable and potentially suitable to improve the performance of Lithium-Air battery operated with dual electrolytes.
CHAPTER ONE

INTRODUCTION, MOTIVATION AND OBJECTIVES

The lithium-air battery systems are electrochemical power sources that have gained attention globally in recent years owing to their exceptionally high theoretical specific capacity and energy density [1] [2]. The potential applications of lithium-air battery range from portable electronics devices to electric vehicles. However, these great potentials are limited by several challenges that have prevented the successful implementation of Li-air battery systems. One of the greatest challenges is the possible reactions involving lithium and air electrode to result in chemical products that lowers the specific capacity and energy density of the battery system. The mentioned problems are highly influenced by the configurations of the electrolytes of the lithium-air battery [3]. Currently, there are four types of electrolyte configurations in Li-air battery system being researched around the world today. They include: 1) the conventional non-aqueous/aprotic electrolyte system; 2) the aqueous electrolyte liquid system; 3) a mixed system with a compound electrolyte system that includes an aqueous electrolyte immersing the cathode and an aprotic electrolyte immersing the anode and a solid electrolyte to separate the liquid electrolytes; 4) all-solid-state battery with a solid electrolyte [4]. Depending upon the configurations of the electrolyte system, the typical problems encountered in the operation of Li-air battery include: the corrosion of Lithium Anode by water and oxygen and the decomposition of aqueous electrolytes for the cases of 2) and 3) the deposition of insoluble discharge products at the air cathode side for case 1) to limit the access of oxygen [1], [5]. Among the different electrolyte configurations, the non-aqueous/aqueous mixed system (case 3) seems promising since it can restrict the access of oxygen to Li anode and meanwhile maintain sufficient oxygen concentration at the air cathode [1]. In such system, a solid state electrolyte should be applied to separate the two electrolytes from intermixing and at the same time behave as a Li-ion conductive membrane. In order to materialize the on-aqueous/aqueous mixed electrolyte system for enhancing the performance of lithium-air batteries, the key is to identify and develop the solid state electrolyte/membranes. Along this line of thought, the past research has made great progress in developing Li ion conducting ceramic membranes, such as LISICON and the NASICON-type ceramics with high Li-ion conductivity [1]. These ceramic materials have a good low oxygen and water permeability. However, the brittleness, the instability of such Li ion
conducting ceramics in aqueous electrolytes and their reactivity with lithium anode makes their implementation in Li-air battery system a difficult task. In this thesis, we proposed a hybrid hydrophobic/hydrophilic polymer membrane to be employed as the solid state electrolyte/membranes for use in the Li-air battery with dual electrolyte configuration. The focus of this research is to develop the process for fabricating Li-ion conductive solid hybrid polymer membranes and investigating their performance and quality with a great emphasis on water permeability and stability of the membrane in both aqueous and non-aqueous electrolytes [5]. As will be shown later in the experiments and results, the selection of polyvinylidene fluoride (PVDF - a hydrophobic polymer) and polyvinyl alcohol (PVA - a hydrophilic polymer) in this research work to fabricate the hybrid polymer membrane will address the aforementioned stability problems of Li-ion conductive ceramic membranes. In addition, the polymer membrane fabrication is much easier than ceramic membranes, which could significantly reduce the fabrication cost. At this point, there is a need to review the concepts about Li-air battery electrolyte systems and the related electrochemical phenomena, which are relevant to this thesis.
CHAPTER TWO

LITERATURE REVIEW

2.1 Lithium-Air Battery Overview

The theoretical energy density of metallic-air batteries is relatively high when compared to other rechargeable batteries. Unlike other conventional rechargeable batteries, the cathode active material in metallic-air batteries is not stored in the battery but can be accessed from the environment. This accounts for their extremely high energy density. [1], [6]. Lithium as the anode material for metal/air battery has an outstanding theoretical specific capacity of 3842 mAh/g when compared to 815 mAh/g for Zinc and 2965 mAh/g for Aluminum [1]. Fig. 1 compares different battery systems in terms of the volumetric energy density (Wh/l) and gravimetric energy density (Wh/kg) together with their respective relative weights and sizes. The high performance of lithium air battery has attracted attention for commercial use as functional rechargeable battery system. However, the poor charge-discharge cycle ability and its potential lithium anode corrosion have hindered the further development of cells with metallic lithium as anode materials [7]. Basically, the essential reaction at Lithium anode is

\[ Li \xrightarrow{\text{charge}} Li^+ + e^- \]  

(1)

Although the above reaction at Lithium anode appears simple, owing to some critical issues, it has been very difficult to implement Li anode with rechargeability for practical application. To obtain a satisfactory performance for metallic Li anode, it is necessary to employ the right strategies to solve these crucial issues. The vital strategy here is to optimize the chemical and physical interfacial structures between Lithium and electrolyte used. In this regard, the key is to select appropriate electrolyte system to achieve high charge/discharge efficiency and provide adequate safety features [8]. Next, we will review the most commonly used electrolyte configurations in Lithium battery system.
Figure 2.1.1: The gravimetric energy densities (Wh/kg) for various types of rechargeable batteries compared to gasoline. The theoretical density is based strictly on thermodynamics and is shown as the blue bars while the practical achievable density is indicated by the orange bars and numerical values. For Li-air, the practical value is just an estimate. For gasoline, the practical value includes the average tank-to-wheel efficiency of cars.[4]

### 2.2 Configurations of electrolyte systems in Li-air Battery

There are basically four different kinds of configurations or architectures of Li-air battery electrolyte systems. All four systems use Li metal as anode and oxygen as cathode material. The reaction mechanisms in each system are dependent upon the electrolyte used. Three of these configurations are based on liquid electrolytes while the fourth one is an all solid-state electrolyte system. They include the following:

i) Nonaqueous (aprotic) electrolyte system.

ii) Aqueous electrolyte system.

iii) All solid-state electrolyte system.

iv) Hybrid (non-aqueous/aqueous) electrolyte system [4], [6].

Each one of these configurations offers certain advantages of its own but also has some technical challenges. It remains an open question which configuration is the best choice in a given design of Li-air battery system.
2.2.1 Nonaqueous (aprotic) electrolyte system:

The non-aqueous electrolyte system used in Li-air battery has a similar configuration to that of conventional Li ion batteries. That is, in both battery systems, the electrolyte is formed by dissolving Li salts in aprotic solvents. However, in addition to this similarity, there is also a significant difference between the electrolyte systems in Li-air and Li ion batteries. In Li-air battery, the electrolyte is in an open environment, since it needs to acquire oxygen from the air. To prevent the nonaqueous electrolyte from contamination by water/moisture in the ambient environment, an air dehydration membrane is required on the cathode side [6].

Figure 2.2.1: Schematic cell configurations for the four types of Li-air battery electrolyte systems.[6]
Figure 2.2.1.1: Schematic operation proposed for the rechargeable aprotic Li-air battery for Discharge and Charge Periods.

The non-aqueous or aprotic electrolyte system used in Li-air battery was first introduced in 1996 by Abraham et al. The testing cell was basically consisted of a lithium metal anode, a dissolved lithium salt in an aprotic solvent as electrolyte, and a porous O₂-breathing cathode and catalyst particles as Air cathode[1], [4]. In such configuration, the critical electrochemistry involves oxygen reduction reaction that occurs at the anode during discharge of the cell. In the discharge process, electrons flow through the external circuit and lithium ions are generated and transported to cathode to react with the reduced oxygen to form Li₂O (and possibly Li₂O₂) [1][4]. Typically, with lithium superoxide LiO₂ as the first product, the oxygen reduction reaction proceeds in a stepwise fashion to form O₂⁻, O₂²⁻, and O²⁻ as the products. The reactions are kinetically irreversible or quasi-reversible electrochemical processes, which as a result yields high polarization for the oxygen evolution reaction. [6] The two possible full cell reactions operated in a Li-air battery are as follows:

\[ 2Li + 1/2O_2 \rightarrow Li_2O \]  \hspace{1cm} (2)

And

\[ 2Li + O_2 \rightarrow Li_2O_2 \]  \hspace{1cm} (3)

The reversible cell voltage is 2.959V for reaction (2) and 2.913V for reaction (3).
The full reduction of $O_2$ to $Li_2O$ (cell reaction (2)) is desired, since it gives a higher specific energy and energy density, though, in practice, but it appears that $Li_2O_2$ forms more readily than $Li_2O$.

The half-cell reactions for Li–air cell are given as follows:

$$Li(s) \leftrightarrow Li^+ + e^- \quad \text{(anode reaction) (4)}$$

$$Li^+ + 1/2 O_2 + e^+ \leftrightarrow 1/2 Li_2O_2 \quad \text{(cathode reaction) (5)}$$

$$Li^+ + e^- + 1/4 O_2 \leftrightarrow 1/2 Li_2O \quad \text{(cathode reaction) (6)}$$

Unlike the cathode reaction (5 or 6), the anode reaction (4) is reversible. The reversibility of cathode reactions (5) and (6) is not a prerequisite but a necessary condition for the Li–air battery to be rechargeable.[1]

With the nonaqueous electrolyte configuration, the lithium anode is in contact with the electrolyte to form a stable SEI (solid electrolyte interface) interfacial layer. The stable SEI offers a protection layer that prevents the further reaction of Li anode with the electrolyte and reduces the formation of dendrites. Examples of electrolytes employed as aprotic or non-aqueous for this configuration includes: organic carbonates (ethylene carbonate, propylene carbonate, dimethyl carbonate), ethers (tetrahydrofuran(THF),dioxolane),and esters(γ-butyrolactone),which solvate lithium salts, such as $LiPF_6$, $LiAsF_6$, $LiN(SO_2CF_3)_2$, and $LiSO_3CF_3$ and have high oxidative stabilities[11].

The benefits of using non-aqueous electrolytes are to suppress the anode corrosion, enhance the Li–air cell voltage (up to a theoretical value) to result in increase in the cell specific energy. There are however drawbacks in using the non-aqueous electrolyte, since the discharge products ($Li_2O_2$ and/or $Li_2O$) are insoluble in the non-aqueous electrolyte. The insolvability of discharge products causes a buildup of discharge products on the cathode surface to inhibit the flow of reactants ($O_2$, Li ions, and electrons) to the active surface. As a result, this probably lowers the discharge capacity (much lower than theoretical capacity) of the Li-air. With exclusion of construction materials but including lithium anode and carbon cathode with 70% porosity, the cell capacity are estimated as 2790 Whkg$^{-1}$ and 2800 WhL$^{-1}$ [2], [6]. Another disadvantage of using nonaqueous electrolyte in Li-air battery is related to the poor solubility of $O_2$ in the electrolyte. This has adverse effects to limit the high rate capacity of the cell. In addition, the
overall cell impedance can be increased due to and the passivation of the positive electrode by an electronically insulating discharge product.[4]

**2.2.2 Aqueous electrolyte system:**

The Li-air cell with aqueous electrolyte to transport the ionic charge carriers are made up of the protected Li metal anode, aqueous electrolyte, and air cathode. In such system, the electrolytes are called active material because they are consumed in the course of discharge –charge processes. [1] In addition, the pH value of the aqueous electrolyte is important in influencing the reactions of Li with O₂.

In acidic electrolyte media (pH < 7.0), the full cell reaction is:

\[2Li + 1/2 O_2 + H^+ \rightarrow 2Li^+ + 2H_2O\]  \hspace{1cm} (7)

An example of the acidic electrolyte such as in sulphuric acid monohydrate, the full cell reaction, in which a conjugate base is produced, is given by:

\[4Li + 2(H_2SO_4.H_2O) + O_2 \leftrightarrow 2Li_2SO_4 + 3H_2O\]  \hspace{1cm} (8)

In alkaline electrolyte media (pH > 7.0), the full cell reaction is:

\[2Li + 1/2 O_2 + H_2O \rightarrow 2LiOH\]  \hspace{1cm} (9)

In alkaline aqueous environment, e.g., diluted LiOH solution, the product of O₂ reduction is LiOH. At standard temperature and pressure, the solubility limit of LiOH in water is about 5.25 M. If the concentration of LiOH exceeds its solubility limit, it will precipitate out of the aqueous solution as a monohydrate, LiOH·H₂O, rather than LiOH as shown below: [12][4]

\[4Li + 6H_2O + O_2 \leftrightarrow 4LiOH\cdot H_2O\]  \hspace{1cm} (10)
In comparison to nonaqueous electrolyte configuration, the Li–air cell with aqueous electrolytes shows relatively lower specific energy. The highest specific energy and energy density for Li–air cell in alkaline aqueous electrolyte have been estimated as 1300 Whkg$^{-1}$ and 1520 WhL$^{-1}$, respectively. The Li–air cell with acidic electrolyte has slightly higher specific energy and energy density, which have been estimated as 1400 Whkg$^{-1}$ and 1680 WhL$^{-1}$, respectively. In the estimation of the specific energy and energy density, the construction materials—for example current collector, casing, etc. were not included [2]. The half-cell reaction of Li-air battery in aqueous electrolyte configuration is summarized as follows:

At the cathode: \[ O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^- \] (11)
At the anode: \[ Li \leftrightarrow Li^+ + e^- \] (12)

In the course of discharge process, \( O_2 \) is electrocatalytically reduced to produce hydroxyl ions (OH$^-$) at the cathode (Equation 10); while Li$^+$ ions are produced at the anode (Equation 11) as a result of Li metal oxidation. The discharge product LiOH is soluble in water and can precipitate to form LiOH·H2O when its concentration is above the solubility limit (5.25 M at 25°C) [12]. During the charge process, \( O_2 \) gas is created at the cathode and Li is plated at the anode. In typical, the electrocatalytic reduction of \( O_2 \) in aqueous solution often needs the use of costly catalysts to improve the reaction kinetics. For example, Pt catalysts are commonly used in Li-air battery with acidic electrolytes. [15][16]. Similar to the nonaqueous Li/air cell, the rechargeable aqueous system is also at development stage, and new designs continue to be discovered. The main benefits of the aqueous electrolyte based Li-air battery are that the discharge reaction product is soluble in water. As a result, the passivation of air electrode, which is a problem in nonaqueous electrolyte based Li-air battery, is not a great concern anymore. Additionally, the selection of appropriate aqueous electrolyte system to achieve reversible charge-discharge Li-air cells does not appear to be a serious problem. Conversely, the effective storage of discharge product, the stability of separator against both Li anode and aqueous air electrode, and the use of costly catalysts remain a considerable challenge.

The first Li-air battery prototype with an entire aqueous electrolyte system was developed by Polyplus Co in 2004. [14]. In the disclosed cell design and fabrication, the Li metal anode was protected by a layer of glass-ceramic materials - LiSICON and/or LiM$_2$(PO$_4$)$_3$. The ceramic
protective layer is ionically conductive and able to prevent Li metal from a vigorous reaction with water and provide the anode stability in the aqueous electrolyte [13]. The operating principle of the aqueous Li-air cell developed by Polyplus is shown schematically in Figure 2.2.2.1.

![Diagram of Polyplus aqueous Li/air cell](image)

Figure 2.2.2.1: Cross section of Polyplus aqueous Li/air.[3]

### 2.2.3 All solid-state electrolyte system:

Lately, an all solid-state Li-air battery was developed by Kumar et al [20]. The cell is composed of Lithium metal anode, a Li-ion conductive solid electrolyte membrane fabricated by laminating glass-ceramic and polymer-ceramic materials, and a solid-state composite air cathode prepared from high surface area carbon and ionically conductive glass-ceramic powder. The principle of operation of the solid-state Li-air cell is shown schematically in Fig 2.2.3.1. The full cell reaction for the all-solid-state battery is most likely similar to that for the aprotic electrolyte based Li-air battery, which can be expressed as:

\[
2Li + O_2 \leftrightarrow 2Li_2O_2 \quad E_0 = 3.10V \quad (13)
\]

During the discharge, \(Li_2O_2\) is produced at the cathode. In the course of charge process, lithium is plated onto the metallic lithium surface. The solid-state Li-air battery is believed to be promising because the reactivity of lithium and the associated safety concerns have been
resolved. In such configuration, the solid-state electrolyte (mostly inorganic electrolyte) is able to isolate lithium from moisture and atmospheric gases and also to prevent dendritic shorts [20].

Figure 2.2.3.1: A schematic of the Li–O₂-cell and its component materials are shown. The electrolyte laminate is composed of PC(Li2O), GC, and PC(BN) membranes. The PC(Li2O/BN) couples with lithium, which is protected by aluminum foil and used as a current collector. The current collector on the cathode side is a metal cell casing not shown in the schematic [20].

2.2.4 Hybrid (non-aqueous/aqueous) electrolyte system:

As mentioned previously, in both non-aqueous and aqueous configuration based Li-air battery the ideal electrolytes should possess high oxygen solubility and oxygen diffusivity to provide sufficient oxygen flow inside the air cathode. However, such a desired characteristic is actually in conflict with the necessity to prevent oxygen access to the lithium anode. It is hard to reconcile such conflict in the conventional rechargeable battery with only one kind of electrolyte such as aqueous, organic, or solid-state electrolyte. Research strategies to solve this problem have given birth to the introduction of hybrid Electrolyte. The conventional hybrid electrolyte design usually makes use of two electrolytes, A and B (A/B), which may be solid/liquid or solid/solid. Other hybrid electrolyte design includes three electrolytes, A, B, and C (A/B/C). These electrolytes may include the following combinations: solid/liquid/solid or liquid/solid/liquid. Figure 2.2.4.1 shows the structure of these A/B and A/B/C hybrid electrolyte
arrangements. The liquid electrolytes may possibly be aqueous or organic. The solid electrolytes can be LISICON, NASICON, and polymers [18].

Figure 2.2.4.1: Images of (a) A/B and (b) A/B/C hybrid electrolytes [18]

The organic/LISICON/aqueous hybrid electrolytes have been developed and reported recently [18]. This new hybrid electrolyte system integrates the solid-state electrolyte LISICON with traditional organic and aqueous electrolytes. LISICON is employed here as a solid-state separator to selectively separate the ions in the anode and cathode regions. With such hybrid electrolytes being implemented in Li battery, only lithium ions can pass between organic and aqueous areas through LISICON. The operating mechanisms of hybrid electrolyte-based batteries are illustrated in Figure 2.2.4.2.

Figure 2.2.4.2: Schematic representation of the operating mechanism of batteries based on a Hybrid electrolyte
As schematically shown in Figure 2.2.4.2, in hybrid electrolyte-based batteries, the electromigration takes place with two kinds of charge carrier’s mediums (electrolytes) in order to produce a current. This concept is comparable to that of a relay race. The analogy here is that the charge drifting through the hybrid-electrolyte battery as the baton and the charge carrier mediums are the runners.

The hybrid electrolyte in Li-air cell typically consists of two layers with dissimilar properties.[1] The electrolyte in contact with the air cathode has high oxygen solubility and diffusivity to allow for adequate oxygen passage to catalyst centers; and the electrolyte in contact with the Li anode is able to restrict oxygen access to reduce the anode corrosion problem.

Following this line of thought, Polyplus developed a hybrid electrolyte based Li-air battery, which has a cell structure of Li anode//non-aqueous electrolyte/ionic conducting glass-ceramic membrane/aqueous electrolyte//air cathode. Lately, Zhou’s group [3] presented a Li-air battery system including an organic/aqueous hybrid electrolyte. The basic battery chemistry involves the catalytic reduction of O\textsubscript{2} at the cathode that occurs in an aqueous electrolyte such as diluted LiOH solution; and the oxidation of lithium anode remains in a nonaqueous (organic) electrolyte. The nonaqueous and aqueous electrolytes are separated by a solid Li-ion conductive membrane [17], [18] [5]. The Li-ion conductive membrane could consist of a SPE (Solid Polymer Electrolyte) with satisfactory properties [60] and Li\textsuperscript{+} conducting glass ceramics such as LIC-GC, LISICON, and NASICON. These types of materials have a satisfactorily low oxygen and water permeability [15]. The Li-ion conducting membrane could also be a combination of LISICON and SPE [19][20].

The overall reaction for the hybrid electrolyte based li-air cell can be written as:

\[
4Li + O_2 + 2H_2O \leftrightarrow 4LiOH \quad (14)
\]

The discharge product produced at the surface of porous carbons at the air electrode is LiOH which can be dissolved in water. The maximum concentration of Li\textsuperscript{+} and OH\textsuperscript{-} ions is determined by the solubility of LiOH in water, which is 12.5 g of LiOH/100 g of water (H\textsubscript{2}O) at 25°C. Akin
to the aqueous electrolyte configuration, when \( \text{Li}^+ \) and \( \text{OH}^- \) concentrations exceed the solubility limit, \( \text{LiOH.H}_2\text{O} \) will precipitate to fill up the porous volume in the air electrode and finally block the \( \text{O}_2 \) channels and eventually stop the discharge process. To avoid the precipitation of \( \text{LiOH} \), more \( \text{H}_2\text{O} \) should be added or circulated in the cell operation. Figure 2.2.4.3 schematically shows the operating principle of a Li-air cell with non-aqueous/membrane/aqueous hybrid electrolyte as the electrolyte configuration. Figure 2.2.4.4 shows a similar type of rechargeable lithium-air battery that uses an aqueous/LISICON/nonaqueous hybrid electrolyte as the electrolyte configuration [18].

Figure 2.2.4.3: Diagram showing the operational principle of a rechargeable Li-air battery using dual electrolytes [5]
2.3 Li-ion conducting solid Electrolyte membrane review

Protection of the Li-metal anode from water is the most critical point to achieve long term stability for Li-air batteries. This is especially true for some practical applications, e.g., electric vehicles, in which air containing moisture is used to supply oxygen [21]. One approach to address this problem in rechargeable Li-based cells is to develop mechanically robust solid-electrolyte membranes capable of conducting Li-ions. The Li-ion conductivity of the solid electrolyte membranes must be sufficient over the operating temperature range of the cell to permit a satisfactory current density. Typically, the Li-ion conductivities above 0.1 mS/cm or even greater than 1 mS/cm are desirable at room temperature. In addition, the membranes should have negligible electronic conductivity and high elastic modulus to inhibit Li dendrite initiation [3]. Most importantly, the membrane should be chemically stable with regards to both anode and cathode materials. In addition, it should also be stable with the liquid electrolytes, catalysts, reactive species such as oxygen molecules and reaction intermediates, and water (in aqueous cells).
Certainly, the readily availability of chemical constituents and ease of fabrication are also major concerns for making cost efficient solid-electrolyte membranes. [22] [23]

There are generally two classes of Li-solid electrolytes: inorganic ceramics and organic polymers. The most apparent dissimilarity between these two different types of Li-solid electrolytes is the mechanical properties. Ceramics have high elastic moduli and are hence more appropriate for rigid flat cell designs, such as thin-film-based devices. On the other hand, the low elastic moduli of polymers are suitable for flexible battery designs. Polymers are also usually at ease to process than ceramics, which helps to reduce the fabrication costs. Conversely, ceramics are more appropriate for high temperature or other aggressive environments. Ionic conductivity is considered of great importance when it comes to fabrication of electrolyte materials [24]. Several inorganic compounds (sulfides, oxides, phosphates) in crystalline, polycrystalline or amorphous morphologies, along with solid dense polymer-based materials, have been investigated with conductivities at room temperature ranging from $10^{-8}$ to $10^{-2}$ S/cm (see Figure 2.3.1). [14][25] [26][27]. Solid-state electrolytes usually have smaller conductivities than liquid electrolytes. The difference is typically no less than 1 - 2 orders of magnitude. It is noted that, in solid-state systems, of the transport of Li ions is a thermally activated Arrhenius-type process. As a result, the conductivity increases with temperature. In some instances, the conductivity can be increased by two orders of magnitude when temperature changes from 0 to 200°C. For this reason, operating a Li-air cell at elevated temperature (>80°C) may increase the rate capability and capacity. Nevertheless this could also create numerous engineering challenges at the system level.
2.3.1 Ceramic Electrolytes:

Ionic conduction in ceramic electrolytes is due to the creation and/or movement of ionic point defects, which requires energy. As a result, the conductivity of these ceramic electrolytes increases with temperature. In general, ceramic solid electrolytes are well appropriate for high-temperature applications. Nevertheless, in some compounds, the ionic conduction is practically high even at quite low temperatures. There are numerous types of lithium-ion conducting inorganic ceramics that have been examined for use in lithium batteries [28], [29]. One of the major advantages of the inorganic solid electrolytes is that these materials are typically single ion conductors. This means that only the Li ions have a considerable mobility, and the anions and other cations form a rigid framework. Such a character has many favorable consequences such as eliminating the anionic concentration gradient across the electrolyte. This may help subdue unwanted side reactions or decomposition of the electrolyte.
The conductivity of solid electrolytes is usually limited by grain boundaries. The grain boundary contribution to total resistance is usually delicate to the ceramic composition and determined by foreign phases that precipitate at the boundaries. There is therefore a need to understand and optimize the grain boundary contribution in order to make progress in improving ionic conductivity of a ceramic polycrystalline material. To fully understand the limitations of bulk transport, it is necessary to synthesize and carry out transport measurements on single crystal samples, which is usually very challenging. An alternative route is by first-principles computations and molecular dynamics simulations, which has proven useful to comprehend the transport mechanisms at atomic-level. After understanding the fundamental transport limitations for a given material, it is then critical to engineer the structure and fine-tune the synthesis methodology to enhance the microstructure and thus the conductivity.

Sulfides
Sulfide compounds in crystalline, amorphous and partially crystalline morphologies have been employed as lithium-ion conductors. For instance in Li₂S–P₂S₅ glass or glass–ceramic, the maximum conductivity occurs at 20–30% P₂S₅ and is determined by the degree of crystallization [30–32]. Glass–ceramics have conductivities (i.e. after crystallization) that are higher than those of the equivalent glasses at lower temperatures, which shows that the crystalline phase presents high conductivity and lower activation energy than the amorphous phase. However this is not the case all the time. In some other sulfide glasses (e.g. Li₂S–P₂S₅–Li₄SiO₄[32]), it has been observed that crystallization reduces conductivity. Another example of sulfide glasses is Li₂S–SiS₂ with conductivity similar to that of Li₂S–P₂S₅. With addition of lithium silicate (Li₄SiO₄) the conductivity of Li₂S–SiS₂ can be further improved. Similar phenomena were also observed for Li₂S–Ga₂S₃–GeS₂, which has similar or lower conductivity than Li₂S–P₂S₅ but can be improved with the addition of lithium silicate (Li₄SiO₄). Li₂S–Sb₂S₃–GeS₂, on the other hand, has a lower conductivity than Li₂S–P₂S₅. It was also observed that crystalline Li₃.25Ge₀.25P₀.75S₄ has a high conductivity, which is in the similar range as those of Li₂S–P₂S₅ glass–ceramics, but the conductivities of Li₄₂Ge₀.₈Ga₀.₂S₄ and Li₂₂Zn₀₁Zr₁₀S₃, are lower than those of Li₂S–P₂S₅ glass–ceramics. It was reported that the oxygen additions to Li₂S–GeS₂ increases the room
temperature conductivity [39]. The increase is accredited to an rise in the coordination number of lithium, but increasing volumes of oxygen added will cause a drop in free volume, resulting in a reduction in conductivity. Li Super-Ionic Conductors (LiSICONs) has been a popular ceramic electrolyte. They are usually \( \text{Li}_{3}\text{PO}_4 \) type oxysalts [26], [33] (for example \( \text{Li}_{14}\text{Zn}()\text{GeO}_4 \)) that comprise of interstitial Li ions. LiSICONs normally display a reduction in conductivity over time when temperature is low due to Li trapping by the immobile sublattice through defect complex creation.[26], [35]. The conductivity at room temperature is normally less than \(10^{-4}\text{S/cm.}[26]\). Thio-LiSICON, the S analog to LiSICON (for example \( \text{Li}_4\text{GeS}_4 \)), can achieve high conductivity and low activation energy at room-temperature (e.g., \( 2.2 \times 10^{-3}\text{S/cm} \) and \( 20 \text{kJ/mol} \) for \( \text{Li}_{3.25}\text{Ge}_0.25\text{P}_0.75\text{S}_4 \)). Furthermore, Glass ceramics with associated structures to thio-LiSICON display even improved performance (\( 3.2 \times 10^{-3}\text{S/cm} \), \( E_a = 12 \text{kJ/mol} \) for \( 70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5 \)). In comparison, crystalline (glass) ceramics have approximately an order of magnitude higher conductivity at room temperature than their amorphous counterparts (glasses) for these systems, even though there are several exceptions to this trend[24]. Given the high conductivities (\( 10^{-3}\text{S/cm at room temperature} \)) of ceramic solid electrolyte, one should not ignore their disadvantages - difficult to fabricate and poor chemical stability[38].

**Oxides**

In comparison to GeS2, GeO2 has smaller conductivity. Given the lower conductivity of oxides when compared with sulfides, the oxides in some other systems are still good lithium-ion conductors. Perovskite \( \text{Li}_3\text{La}_{2-3\gamma}\text{TiO}_3 \) (LLTO) is a very promising lithium-ion conducting oxide [40]. The maximum conductivity has been observed at \( y=0.125 \) (La/Li=1.4) [41], [42]. This complies with the molecular dynamics calculations that showed a maximum conductivity at \( y=0.105 \) and minimum conductivity at \( y=0.045 \) [43]. At lower lithium contents (small \( y \)), usually at \( y \approx 0.08 \), an orthorhombic phase rather than the tetragonal phase is formed, which exhibits higher conductivity [44]. Higher conductivities in LLTO are also achieved by adding small amounts of aluminum to replace titanium. With addition of sodium additives, it results in a reduced conductivity. The conductivities of LLTO are not significantly affected by the replacement of oxygen with fluorine. Additional studies indicate that silica additives to \( \text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3 \) increases total conductivity, because of its effect on grain boundary transport [45]. It has been reported that LLTO mixed with LiMn2O4 to forms a composite cathode [46].
Garnet-based oxides based on Li$_5$La$_3$Ta$_2$O$_{12}$ are similar to those of LLTO in terms of conductivity values. Ceramics belonging to the garnet family have lower conductivity than NaSICON-type phosphates and perovskite-type oxides ($8\times10^{-4}$S/cm at 300 K [47]). However, they exhibit a lower grain boundary resistance and possess higher chemical stability against Li metal.[33].

**Phosphates**

Several phosphates are comparable to sodium-ion conducting NASICON compounds. They are good lithium-ion conductors. Initial work on the Li analog to NASICON, LiM$_2$(PO$_4$)$_3$, led to innovations of some materials with high conductivity but not chemically stable against Li (M = Ti[24], [48]), or otherwise with good stability but poor conductivity (M = Ge[24]). It was observed that, through solid state reactions with Al substitution, Li$_{1+x}$Al$_x$Ge$_{2-x}$(PO$_4$)$_3$ or LAGP has been developed with 4 orders of magnitude higher conductivity.[49]

The Ohara group discovered that by heat treatment of Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$, or LTAP, glass ceramics including a NaSICON crystalline phase were obtained and exhibited high conductivity up to $1.3\times10^{-3}$S/cm.[38], [50]. The material is stable in aqueous solutions as well as when in contact with Li metal. Also his makes it an appropriate candidate for aqueous Li-air cells. Recent studies also revealed that LTAP is stable in acidic solutions.[51] Yet, this material tends to be difficult to fabricate with large area and low thickness.

The Bates group presented using radio frequency magnetron sputtering of lithium silicates, phosphates, or phosphosilicates to incorporate N$_2$ to form LiPON, an amorphous analog to LiSICON.[52] Thin-film batteries with Li as anodes and Lithium Phosphate OxyNitride (LiPON) as separators have proven thousands of cycles.[53], [54] Nevertheless, the low conductivity of LiPON ($2\times10^{-6}$S/cm at 5°C[52]) disqualifies the development of cells with thick LiPON membranes.

Zirconia-based phosphate, LiTi$_{0.5}$Zr$_{1.5}$(PO$_4$)$_3$, have bulk conductivity lower than that of LTAP. The impedance spectroscopy studies of LiTi$_{2-x}$Zr$_x$(PO$_4$)$_3$ demonstrated that the addition of zirconium influences the bulk conductivity more than the grain boundary conductivity [55]. Zirconia-based phosphates, e.g. Li$_x$AlZr[PO$_4$]$_3$, are being investigated for higher temperature applications [56]. The low conductivity of lithium phosphate glass can be increased with
aluminum or halogen salts additives. Glasses with Li$_3$Fe$_2$(PO$_4$)$_3$ crystals have been claimed as the possible electrolyte materials[57].

Li$_3$N are promising ceramic electrolytes with high conductivity ($\sim$10$^{-3}$S/cm at room temperature). However, it is unstable at high potentials (>0.445 V vs. Li). [26][58]. On the other hand, Li$_3$P has an order of magnitude lower conductivity, but it is stable up to 2.2 V.[58], [59] It is worth to mention another ceramic electrolyte known as Li analog to sodium $\beta$-alumina, Li$_2$O·11Al$_2$O$_3$. This novel material exhibits a high room-temperature conductivity of 3×10$^{-3}$S/cm, but it is extremely hygroscopic and difficult to prepare dry [58], [59].

2.3.2 Polymer electrolytes:

Polymer electrolytes are suitable materials for electrochemical device applications, such as high energy density rechargeable batteries, fuel cells, supercapacitors etc. So far polymer electrolytes processing has witnessed different developmental stages which ranges from dry solid polymer electrolyte (SPE) systems to plasticized, gels, rubbery to micro/nano-composite polymer electrolytes. Unlike the polymer gel electrolytes, which incorporates organic solvents and demonstrate reasonable room temperature conductivity as high as $\sim$10$^{-3}$Scm$^{-1}$, the dry SPEs still suffer from poor ionic conductivity lower than 10$^{-5}$Scm$^{-1}$. A number of approaches have been explored to enhance the room temperature conductivity in the vicinity of 10$^{-4}$Scm$^{-1}$ in addition to improving the mechanical stability and interfacial activity of SPEs.

In comparison to ceramic electrolytes, polymer electrolytes offer advantages over ceramics including good processibility and flexibility, dimensional stability, safety and the ability to prevent lithium dendrite formation [36], [52–54]

The most frequently used polymer electrolytes is poly (ethylene oxide) (PEO). In addition to PEO, others including for example poly (methyl methacrylate) (PMMA), PVDF (Polyvinylidene fluoride), PVA (Polyvinyl alcohol), etc., were also used as polymer matrixes to develop various solid polymer electrolytes (SPEs). [60]

It is of importance to mention that there has been a prejudiced conception that fast ion transport in SPEs was primarily due to the presence of amorphous phase in the polymeric host. In view of that, it was assumed that the higher the fraction of amorphous phase, the greater would be the ionic conduction in SPEs [21]. In order to ensure a good flexibility of the polymer chains supporting faster ion transport, as a result, key research investigations in the past were directed
towards producing enormous and stable amorphous phase in the polymeric hosts of low glass transition temperatures (Tg). However, this conventional conception has lately been reversed by Gadjourava group [22] who has experimentally established that the static and ordered crystalline environments in the polymer host may possibly also support high ion conduction in SPEs as discussed below.

For optimum performance of SPEs, listed below are properties that SPEs should exhibit:

- Ionic conductivity of $\sigma \geq 10^{-4}\text{Scm}^{-1}$ at room temperature. This conductivity allows us to achieve a performance level near that of the liquid electrolyte-based devices.

- Ionic transference number $t_{\text{ion}} \sim 1$. This is not only absolutely necessary. If possible, the polymer electrolyte should be a single-ion (namely, cation) conducting system. For battery applications, the polymer electrolyte should flawlessly perform as anion conducting medium and as an electronic insulator. Nevertheless, the majority of the polymer electrolytes reported so far, although demonstrating negligible electronic conduction has cationic transference number $\leq 0.5$. This is suggestive of the fact that, at the extreme, only half of the available transporting ions move in the polymer electrolytes [61–63]. Apparently, the larger the cationic transference number (close to unity), the smaller would be the concentration polarization effect in the electrolytes during charge–discharge steps, and thus, the higher the power density would be reachable in the battery [64].

- Satisfactory chemical, thermal and electrochemical stabilities. The solid state electrochemical devices are fabricated by inserting the polymer electrolyte membranes between appropriate cathode and anode materials. In order to avoid undesired chemical reactions proceeding at the electrode/electrolyte interfaces, the polymer electrolytes should have an extraordinary chemical stability. Moreover, to ensure a wider temperature range during battery operations, polymer electrolytes ought to be thermally stable. They should also possess a good electrochemical stability window extending from 0V to as high as 4–5V.

- High mechanical strength. The polymer electrolytes must be mechanically stable to facilitate the scaling up and large-scale production of the devices.

- Compatibility with the electrode materials. Lastly, the polymer electrolytes have to be compatible with a variety of electrode materials. Currently, major work has been diverted
to discovering such non-toxic anode/cathode materials which would improve the performance level of the electrochemical devices [65].

SPEs offer great possibilities of making flexible, light-weighted high/low energy density all-solid-state primary/secondary batteries with reasonable long shelf-life and wider operational temperatures. At the moment, great numbers of rechargeable batteries based on Li$^+$ ion conducting polymer electrolytes membranes are being mass-produced on a commercial scale. It is also proposed that SPEs will be promising as Li-ion conducting electrolyte membrane in the proposed hybrid electrolyte configuration for rechargeable Li-Batteries. With a focus on materials synthesis, a general preview about the development of polymeric electrolytes in the last 20–30 years particularly in is listed below. The fabrication methods extensively used to cast polymer electrolyte membranes, characterization of the material/ion-transport properties, and their application as hybrid electrolytes in rechargeable batteries will be discussed in the subsequent section. [65]

2.3.2.1 Polymer electrolyte materials designing and broad classification

With the main objective to synthesize polymer electrolytes with ionic conductivity at room temperature near that of liquid/aqueous electrolytes, the first ion conducting polymeric material was discovered in 1973. [66] . Since then, the materials design for improving polymer electrolytes has undergone several stages. Several polymer electrolyte systems, comprising a selection of transporting ions, namely, H$^+$, Li$^+$, Na$^+$, K$^+$, Ag$^+$, etc, are at present identified today. Table 2.3.2.1.1 lists the chemical formulae and thermal characteristics, such as, glass transition ($T_g$)/melting point ($T_m$) temperatures of a few certain polymers, which are normally used as hosts for the complex selection of ionic salts and/or synthesis of ion conducting polymers. On the basis of preparation routes adopted as well as on their physical conditions, the polymer electrolyte materials have been categorized into following general types [67], [68]

(i) Conventional polymer–salt complex or dry SPE.

Dry SPEs are synthesized by complexing/dissolving ionic salts into coordinating polar polymer hosts, such as, poly (ethylene oxide) (PEO), poly(propylene oxide) (PPO), etc [65]. The casting of film/membrane is prepared either by the conventional solution cast method or by a recently embraced novel hot-press technique. The film casting methods are discussed briefly below.
Table 2.3.2.1.1: Some selected polymers hosts, their corresponding chemical formulae and $T_g/T_m$ values [65].

<table>
<thead>
<tr>
<th>Polymer host</th>
<th>Repeat unit</th>
<th>Glass transition temperature $T_g$ (°C)</th>
<th>Melting $T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(ethylene oxide)</td>
<td>$-(\text{CH}_2\text{CH}_2\text{O})_n-$</td>
<td>$-64$</td>
<td>65</td>
</tr>
<tr>
<td>Poly(propylene oxide)</td>
<td>$-(\text{CH}(-\text{CH}_3)\text{CH}_2\text{O})_n$</td>
<td>$-60$</td>
<td>$-^a$</td>
</tr>
<tr>
<td>Poly(dimethylsiloxane)</td>
<td>$-[\text{SiO}(-\text{CH}_3)_2]_n$</td>
<td>$-127$</td>
<td>$-40$</td>
</tr>
<tr>
<td>Poly(acrylonitrile)</td>
<td>$-(\text{CH}_2\text{CH}(-\text{CN}))_n-$</td>
<td>$125$</td>
<td>317</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>$-(\text{CH}_2\text{C}(-\text{CH}_3)(-\text{COOCH}_3))_n-$</td>
<td>$105$</td>
<td>$-^a$</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>$-(\text{CH}_2\text{CHCl})_n-$</td>
<td>$82$</td>
<td>$-^a$</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride)</td>
<td>$-(\text{CH}_2\text{CF}_2)_n-$</td>
<td>$-40$</td>
<td>171</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride-</td>
<td>$-(\text{CH}_2\text{CF}_2)_n-</td>
<td>CF_2\text{CF}(</td>
<td>CF_3)</td>
</tr>
</tbody>
</table>

$^a$ Amorphous polymer.

(ii) Plasticized polymer–salt complex.

These polymer electrolytes are synthesized by addition of liquid plasticizers into dry SPEs in such a way that a compromise between solid polymer and liquid electrolyte occurs. The level of ambient conductivity gets significantly improved by this approach, but at the expense of deterioration in the mechanical integrity of the film along with the increased corrosive reactivity of polymer electrolyte near the metal electrode.

(iii) Polymer gel electrolyte.

Gel electrolytes are generally developed by combining large amount of organic liquid solvent(s)/liquid plasticizers into the polymer matrix capable of forming stable gel. Polymer gel electrolytes also offers high ambient conductivities but undergo related disadvantages previously stated for the plasticized polymer electrolytes [65].

(iv) Rubbery electrolyte.

They are essentially ‘polymer-in-salt’ systems, in dissimilarity to ‘salt-in-polymer’ type SPEs that are the three categories (i)–(iii) mentioned above. In rubbery electrolyte, an enormous quantity of salt is mixed with a small amount of polymer, viz., poly (ethylene oxide) (PEO), poly (propylene oxide) (PPO), etc. The glass transition temperature of these materials is typically low to sustain the rubbery state at room temperature. This facilitates to provide the SPE with high
conductivity. In such SPE system, the complexed/dissolved salts tend to crystallize, therefore, to hinder their usages in practical electrochemical devices [65].

(v) Composite polymer electrolyte (CPEs).

CPEs are fundamentally analogous to the typical two-phase composite solid electrolyte systems. They are likewise prepared simply by dispersing a small fraction of micro/nano-sized inorganic (ceramic)/organic filler particles into the traditional SPE host. SPEs serve as phase I, while filler materials are as the dispersed phase II. The ionic conductivity, mechanical stability and the interfacial activity of SPEs usually get improved significantly because of the incorporation of inorganic (ceramic)/organic filler particles. The size of the filler particles and, hence, their surface area play an important part in enhancing these physical properties [65].

**Casting techniques of Polymer electrolytes films/membrane**

The kind of techniques employed to prepare a SPE membrane depends mainly on the material used and on the preferred membrane structure.

Polymer electrolyte films are generally cast by the following routes:

- Solution cast method.

This is a conventional procedure for casting polymer electrolyte films and gels. This technique entails adding proper quantities of polymer and complexing salt which are dissolved separately in a common solvent, then mixing them together and stirring magnetically for sufficient time to achieve salt complexation with polymer host. For casting CPE films, micro/nano-sized filler particles are added during stirring process. The resulted viscous stock liquor is then poured into a Petri dish for the film formation via slow evaporation of the solvent. Subsequent vacuum drying is further applied for drying the formed SPE films [65].

- Hot-press (extrusion) technique.

This is a unique technique, originally demonstrated by Gray et al [65], [69] and modified recently by several groups with minor adjustments. Hot-press casting has numerous benefits over the regular solution cast method in that it is fast, less expensive, solvent free process for making polymer electrolyte films. This technique involves mixing dry powders of polymer and complexing salt (for casting conventional SPE films) and/or polymer, complexing salt and filler particles of micro/nano-dimension (for casting CPE films) in proper ratio; then the homogeneously mixed powder is heated near the melting point temperature of the host polymer
for adequate time with continued mixing to ensure complete salt complexation. Subsequent press
of the achieved soft lump/slurry between two cold metal blocks/twin-rollers, results in an even,
stable polymer electrolyte film of a few µm in thickness [65], [69].

- Coating

This technique is employed to apply a thin layer of polymer films on a more porous sublayer to
produce a composite membrane. The ion transport and selectivity are derived from the thin top
layer, whereas the sublayer simply functions as mechanical support. A number of coating
techniques can be employed. One type of coating is the interfacial polymerization which
involves the reaction of two extremely reactive monomers (or a pre-polymer) at the interface of
two immiscible solvents. Another type is the dip coating, where an asymmetric sustaining layer
is immersed in a dilute coating solution that contains a monomer, prepolymer or polymer. When
the membrane is removed from the coating solution, a thin layer forms and adheres as a result of
solvent evaporation. Plasma polymerization, in which an ionized gas creates radicals on the
reactants that will form the polymer, was also used for forming very thin and dense top layers.
[69], [70].

- Phase Inversion

The phase inversion process is to transform a polymer from a liquid state to a solid state in a
controlled way. The solidification process is frequently initiated through liquid-liquid demixing.
In the demixing process, one of the liquid phases will solidify to produce the solid matrix. The
membrane morphology, e.g. microporous and nonporous structures, can be tailored by
controlling the initial stage of phase transition. The implementation of phase inversion includes
a variety of different techniques, among which the most common one is by immersion
precipitation. In such process, a polymer solution cast on an appropriate support is then
subsequently immersed in a coagulation bath containing nonsolvent [70].

- Sintering

This technique involves a process where polymer powders are pressurized at elevated
temperatures. Sintering technique is suitable to prepare porous membranes with polymers that
cannot be dissolved in an appropriate solvent, for example, PTFE [70].


- **Stretching**

In this technique an extruded film or foil from a (semi-)crystalline polymeric material is stretched perpendicularly with respect to the extrusion direction. As a result of anisotropic failure modes, small ruptures/cracks can be induced to create polymer membranes with porous structures. [70].

- **Track-Etching**

In this method, a high energy particle radiation is applied to bombard the film through the thickness. Subsequent immersion of the film in a suitable solvent, the bombarded region of the polymer film is etched away to create porous structures. This approach is able to produce cylindrical pores with extremely even pore size distribution.[70].

### 2.3.2.2 Characterization techniques of Polymer Electrolytes

Several analytical techniques have been employed for characterizing polymer electrolyte film. Spectroscopic methods such as FTIR/IR, Raman, etc and/or XRD analysis can be used to verify the salt complexation in addition to checking the dispersion states of filler particles in the host polymer electrolyte. In both crystalline and amorphous phases, the ion–polymer association can be identified by means of monitoring the changes in the vibrational modes. Detailed information on the structural features of polymers such as degree of crystallinity and crystallite size can be deduced from X-ray and neutron diffraction studies. The EXAFS (Extended X-ray Absorption Fine Structure) study reveals the local environment of the ion and also the existence of ion pairs in both crystalline and amorphous phases. In addition, it also helps to find out the bond length of ion–polymer interaction. Another powerful technique is NMR (Nuclear Magnetic Resonance Spectroscopy). On examining the chemical shifts, line widths, relaxation time and self-diffusion coefficient, NMR can be used to probe the immediate neighborhood of the transporting ion. Scanning electron microscopy (SEM) is normally used to provide the surface morphological information of the polymer electrolyte films. The thermal analysis techniques, e.g., DTA/DSC (Differential Thermal Analysis/Differential Scanning Calorimetry), reveals vital insights concerning the degree of crystallinity/amorphosity, glass transition temperature ($T_g$) and melting point ($T_m$), etc of polymeric materials.[65].


Several experimental techniques can be used to measure some basic ionic transport properties of these polymeric materials, such as ionic conductivity (\(\sigma\)), ionic mobility (\(\mu\)), mobile ion concentration (\(n\)), ionic drift velocity (\(v_d\)), ionic transference number (\(t_{\text{ion}}\)). Among them, Electrochemical Impedance Spectroscopic (EIS) techniques are commonly employed for this purpose. In EIS measurements, the impedance values: \(Z'(\text{real})\) and \(Z''(\text{imaginary})\) are evaluated at various frequencies ranging from MHz to mHz and plotted as a complex impedance plot which clearly separates the different resistive contributions such as bulk, grain boundary and electrode/electrolyte interfacial resistance. The EIS technique provides additional insights related to different interfacial phenomena. The ionic mobility (\(\mu\)) and the ionic transference number (\(t_{\text{ion}}\)) can be straightforwardly found out by the dc polarization transient ionic current (TIC) technique [71]. \(t_{\text{ion}}\) gives the extent of ionic contribution to the total conductivity quantitatively. \(t_{\text{ion}} = 1\) in a pure ionic conductor, whereas it varies between 1 and 0 in the mixed (ionic + electronic) systems. The cationic transference number (\(t_+\)) is the major parameter to judge the performance of the electrolytes. The cationic transference number (\(t_+\)) can also be determined by means of combined dc polarization and ac impedance measurements [61]. The other ionic parameters such as \(n\), \(v_d\), can also be estimated with the aforementioned measurements and suitable physical models.
CHAPTER THREE

PROCESSING, STRUCTURE CHARACTERIZATION AND
PERFORMANCE EVALUATION OF HYBRID MEMBRANES-
EXPERIMENTS

3.1 Preparation of Hybrid Membrane

3.1.1 Materials

The hybrid polymer membrane is composed of poly(vinyl alcohol) or PVA on one side and poly
(vinylidene fluoride) or PVDF on the other side. PVA polymer in powder form was purchased
from sigma-Aldrich company with a number averaged molecular weight Mw = 146,000 –
186,000 g/mol and hydrolysis degree of 99%+. PVDF polymer in powder form was purchased
from Polyscience Inc. with a number averaged Mw = 80,000 g/mol. PVA has excellent film
forming and adhesive properties. The PVA is hydrophilic and has a melting point of 230º C.
Unlike PVA, PVDF is hydrophobic with a melting point of 177º C. The hydrophilicity of PVA
and hydrophobicity of PVDF enhance their use as hybrid membrane to separate the aqueous and
organic electrolytes from inter mixing as well as conduct Li ions. This is important in the hybrid
electrolyte configuration employed for enhancing the performance of Li-air batteries. N-Methyl-
2-pyrrolidone (NMP, Sigma-Aldrich) was used to dissolve both PVA and PVDF for polymer
solution preparation.

3.1.2 Processes for making PVA/PVDF hybrid membranes:

Two different approaches, namely phase inversion and solution casting, have been chosen to
process PVA/PVDF hybrid membranes in order to cover a wide range of membrane porosities
and morphologies. In each of these two techniques, PVA and PVDF polymer solutions are
required. To obtain a 5 wt% of PVA or PVDF solution, 5g polymer was dissolved in 100mL of
NMP with magnetic stirring. To improve the polymer dissolution rate, the PVDF/NMP and
PVA/NMP mixtures are heated with hot plate to and maintained at ~100°C and ~150°C respectively. After a visually clear and homogenous solution was formed, the heating process was stopped and the polymer solution was left to cool down to room temperature ready for membrane preparation with either the phase inversion or solution casting technique as described below.

### 3.1.2.1 Phase inversion method

In this technique, the PVDF solution was first casted at room temperature (20°C) onto a glass plate. The wet film thickness was controlled by a box coater, with knife gap adjusted at 50µm. Subsequent to the formation of PVD/NMP wet film, methanol, which is a non-solvent for PVDF polymer, was poured over the thin film to facilitate the solidification/precipitation of PVDF. The precipitated PVDF membrane was further dried in vacuum oven at 40°C for a few hours to obtain a semi-dried PVDF film. With a similar procedure, the PVA solution was subsequently cast on the formed semi-dried PVDF film to prepare PVA/PVDF hybrid membranes. The knife gap was also controlled at 50µm; and methanol was used as a non-solvent. The resulting PVA/PVDF hybrid membrane (wet) was then dried in the vacuum oven at 60°C for several hours to eliminate the residual solvents.

The disadvantages for the phase inversion method to prepare PVA/PVDF hybrid membranes are:
1) it is difficult to control the thickness of each layer of the hybrid membranes; 2) it generally produces a high porosity membrane which is not suitable for the hybrid electrolyte configuration for Li-air battery; 3) this technique intends to give the membrane with uneven and inhomogeneous surface morphology.

### 3.1.2.2 Solution casting method

In order to overcome the disadvantages of phase inversion method mentioned above, we attempted a solution casting method to prepare PVA/PVDF hybrid membranes. This approach involves a sequential casting of PVA and PVDF (5 wt. % in concentration) solutions in a glass mold without using non-solvent. First, a required volume of PVA solution was casted into the glass mold and heated at 80°C for 5 hours to evaporate NMP solvent obtain a desired film thickness of 50 µm. Following the formation of PVA film, a required volume of PVDF solution was subsequently casted onto the PVA film and then heated at 80°C for 12 hours in the vacuum
oven to evaporate the excess solvents for forming the PVA/PVDF hybrid membranes. After a cooling down process, the resulted PVA/PVDF hybrid film can be easily peeled off the mold to give a free-standing membrane, which is then dried again at 40°C for 24 hours in the vacuum oven to remove traces of residual NMP solvent.

With the dimension of the mold (W X L = 5cm X 5cm) used in our process for fabricating PVA/PVDF hybrid membranes, the required volume of polymer solution for making a desired film thickness, e.g., 50 µm, was computed as following:

1) the total mass $M_p$ used for fabricating the polymer film with desired dimension is given by:

$$M_p = D_p \times V_{pf} \quad 3.1a$$

$$M_p = C_p \times V_{ps} \quad 3.1b$$

$$V_{pf} = A_p \times t_p \quad 3.1c$$

Where, $D_p$ is the density of the polymer used, $C_p$ is the concentration of the polymer solution, $V_{ps}$ is the volume of the polymer solution, $V_{pf}$ is the volume of the polymer film, $A_p$ is the surface area of the polymer film, $t_p$ is the desired thickness of the polymer film.

Equation 3.1a and 3.1b respectively give the polymer mass in the dried film and the as-cast wet film, which should be the same if it is assumed that there is no polymer mass loss during the solvent evaporation process.

2) With Eq. (3), the required volume of polymer solution for making a desired film thickness can be accordingly determined as:

$$V_{ps} = \frac{D_p \times V_{pf}}{C_p} = \frac{D_p \times A_p \times t_p}{C_p} \quad 3.2$$

With the known densities of PVA and PVDF given as 1.2g/cm$^3$ and 1.78g/cm$^3$ respectively and $A_p = 5cm \times 5cm = 25cm^2$, the required volume of polymer solution for making a 50 µm PVA and PVDF films was calculated with Eq. 3.2. They are:

$V_{PVA,s} = 3.0ml$ for PVA solution and $V_{PVDF,s} = 4.5ml$ for PVDF solution, respectively.
3.2 Characterization and Property Evaluation of PVDF/PVA Hybrid Membranes

3.2.1 Morphology examination by scanning electron microscopy

Scanning electron microscopy (SEM) was conducted using the Field Emission Scanning Electron Microscope Joel JSM-7401F on PVA/PVDF hybrid membrane for characterizing the film morphologies. The main aim was to observe the pore size and the corresponding size distribution. The SEM was operated at 10 kV accelerating voltage and the membrane samples were coated with gold for enhancing the image quality.

3.2.2 Stability evaluation of PVA/PVDF hybrid membranes

3.2.2.1 Thermal Stability

Thermal analysis was conducted using Differential Scanning Calorimetry (DSC) to gain the knowledge about the thermal transition behaviors of the polymer films prepared in this study. The DSC measurements were performed using a Q100 DSC differential scanning calorimeter (TA Instrument). In a typical DSC run, a total of ~ 7mg of polymer, e.g., PVDF was used. The sample was sealed in an aluminum pan and the temperature was scanned from 0 to 300°C at a scanning rate of 10°C min⁻¹. Figure 3.2.2.1.1 shows a typical DSC curve for PVDF polymers, where melting temperature (B = 177°C) of PVDF is shown.
3.2.2.1.1: Differential Scanning Calorimetry (DSC) temperature sweeping trace for PVDF polymer. Temperature ramping rate was set at 10 °C/min.

3.2.2.2 Stability of PVA/PVDF hybrid membrane in organic and aqueous electrolytes

In order to employ the PVDF/PVA hybrid membranes in a Li-air battery setup, their stability in the accordingly used organic and aqueous electrolytes has to be evaluated. For this purpose, the film samples of PVA and PVDF were immersed in organic electrolyte (1M solution of LiPF6 (Lithium Hexafluorophosphte) in tetrahydrofuran (THF)/propylene carbonate (PC) and) and distilled water and left for 3 days to visualize any possible changes. The mass used in the immersion experiments was 16.70mg and 7.02mg respectively for PVA and PVDF films. In
addition, the film samples experienced immersion testing were subsequently dried in vacuum oven for several hours and measured for mass loss or gain that may be caused by the immersion testing. The testing results indicated that there was no disparity in the masses obtained when compared to their initial masses before immersion.

Similar immersion testing was done for solution processed PVA and PVDF and commercially available melt extruded PVDF films in both diluted LiOH (1M solution of LiOH aqueous electrolyte) and acetic acid (1M solution Acetic acid aqueous electrolyte) solution. After 3 days of immersion in diluted acetic acid solution, there were no visual changes observed for both solutions processed PVA and PVDF samples and the commercial PVDF samples. However, as shown in Chapter 4 – Results and Discussion (figure 4.2.1.1, 4.2.2.1 and 4.2.2.2), the color change has been observed for solution processed PVA and PVA membranes when they were subjected to immersion testing in diluted LiOH solution. In contrast, the commercial PVDF sample showed no visual color changes during the immersion test.

3.2.3 Water/air permeation test of solution processed PVA/PVDF hybrid membranes

3.2.3.1 Preparation of PVA/PVDF Pouch/Bag

For convenience, heat-sealing was applied to further process the as-fabricated PVA/PVDF hybrid membranes into a pouch/bag form. The pouch/bag is easy to use for investigating the water permeation property of the PVA/PVDF hybrid membranes, for setting up Lithium cell for evaluating the Electrochemical Impedance Spectroscopy (EIS) behaviors of the prepared hybrid membranes and for protecting the Lithium metal from being oxidized by air or water. In our studies, the Impulse heat sealer (HPN Iron body 12" Impulse Heat Sealer) was used for making PVA/PVDF pouch/bags. The Impulse heat sealer has heating elements of Nichrome, which is sandwiched between a resistant synthetic rubber and a release fabric coated with Non-Stick PTFE polymer. In the operation of the impulse heat sealer, two pieces of PVA/PVDF hybrid membranes are placed against each other and positioned in place by pressure. With alternatively controlling the on and off of the current pulses that pass through the heating elements, the "heat time" and "cool time" can be separately manipulated to achieve the best sealing effect. To achieve good seal, the processing conditions, which include the time, temperature and pressure, may vary from one material to another. In the PVA/PVDF hybrid membrane case, a setting on
“5” was used, which corresponds to a temperature of 200°C with a heat and cool time of 1 second and 3 seconds respectively.

3.2.3.2 Permeability on solution processed PVA/PVDF hybrid film
Because of the susceptibility of Lithium to oxidation (corrosion) upon exposure to water molecules, it is of great importance for the hybrid membrane to have low water permeability in the development of Lithium cell with hybrid electrolytes. In this study, two approaches were employed to investigate the water permeation properties of the PVA/PVDF hybrid membranes.

Method 1
With the pouch/bag formed by PVA/PVDF hybrid membranes, the water permeation property of the hybrid membranes was qualitatively evaluated with the procedures described below. First, the organic electrolyte (1M solution of LiPF6 (Lithium Hexafluorophosphite tetrahydrofuran) in (THF)/propylene carbonate (PC)) was sealed inside the bag with the PVDF side in contact with the organic electrolyte. Then, it was immersed in water for 4 hours. After immersion, the UV-Vis spectra of the organic electrolyte were taken for examining if there is any water that permeates through the membrane and get inside of the bag. To use this approach, it is critical to establish a baseline on the UV-Vis spectra of the organic electrolyte mixed with water at different concentrations. With inclusion of 0 wt%, 0.1 wt%, 0.5 wt% and 50 wt% of distilled water, the mixture of organic electrolyte/water has been examined with the UV-VIS spectrophotometer (Cary 5000 Varian, Inc) for the baseline establishment. The spectra were taken over the wavelength range from 200 nm to 3000 nm. In the mixture of organic electrolyte/water, it was identified that the absorption peaks occurred at about 2000 nm is attributed to water. With the established baseline and the experimental procedures described above, the water permeation property was determined for PVA/PVDF membranes. A polyethylene bag, which is presumably impermeable to water, was also used for performing the water permeation experiments for comparison. As shown in Figure 4.3.1.1 in Chapter 4 – Results and Discussion. It was observed that the spectra of the samples taken from PVA/PVDF and polyethylene bags were similar to those of the pure electrolyte. This indicates that the PVA/PVDF hybrid membranes prepared in this study has a reasonable resistance to water permeation. However, since it is not directly relevant to the application of hybrid membranes in Li battery setup, this spectroscopy-based
method was not considered an effective way to test the water permeability for the hybrid membranes. For this reason, a second approach was considered.

**Method 2**

In the second approach to evaluate the water permeation property of the PVA/PVDF membranes, lithium foil was sealed inside the bags, which was then immersed in water for several hours. The concept here is that the pristine Lithium metal foil has a shiny smooth metallic surface. When exposed to air, water moisture or water, Lithium can be oxidized. As a result, there will be visual changes on the surface of the Lithium. With this reasoning, it is expected that, the Li ribbon sealed inside the hybrid membrane bag remains shiny same, if the membrane is impermeable to water and air. Otherwise, a visual change occurs if the membrane is permeable to water or Air.

Similar to Method 1, the control experiments were also carried out by sealing lithium foil in polyethylene pouch and immersed in water. It has been observed that, the shiny surface of lithium foil sealed in polyethylene pouch lasted for 2 days before any visual changes occurred. In contrast, the lithium foil sealed in PVA/PVDF bag show apparent visual changes after its immersion in water for several hours. This second method was considered more convincing for an effective water permeability test.

**3.2.4 Stability, water/air permeation test of melt extruded commercially available PVDF films**

The melt extruded commercially available PVDF films were also subjected to the stability and water permeability test. The purpose of testing this melt extruded commercially available PVDF films was to compare the performance of a melt extruded PVDF to that of the solution processed PVDF and PVA films. To distinguish the melt extruded commercially available PVDF films from the solution processed PVDF membranes prepared in this study, from now on, the former sample will be denoted as PVDF (M).
3.2.4.1 Stability of PVDF(M) films
The same procedures for stability test as previously used for solution processed PVA and PVDF films was employed for PVDF(M) films. Unlike the solution processed PVDF and PVA films, the melt extruded PVDF(M) films showed no visual changes in LiOH aqueous electrolyte (1M LiOH aqueous solution), which indicates that the PVDF(M) films was stable in LiOH aqueous electrolyte. The observed difference is presumably due to the residual NMP solvent in the solution processed PVDF and PVA membranes, which is lacking in the commercial PVDF(M) films.

3.2.4.2 Permeability on PVDF(M)/PVA hybrid membrane
The same procedures as described in section 3.2.3.2 – Method 2 was also used to test the permeability for PVDF(M) and PVDF(M)/PVA hybrid membrane bags. It was observed that the PVDF (M) bags offered an improved performance in resistance to water permeability. In comparison to the solution processed hybrid membrane bag, it took a much longer duration for the Lithium foil in PVDF(M) membrane bag to show visual changes. This is an indication of an improved pore structures in PVDF(M) membranes. With the PVDF(M) film as substrate, a similar procedure as described in 3.1.2.2 was applied to fabricate PVDF(M)/PVA hybrid membranes. They were also test for the water permeation properties in two different configurations: 1. solution processed PVA membrane as the inner wall of the bag; 2. PVDF(M) as the inner wall of the bag. It was observed that the PVDF(M)/PVA hybrid membrane bag with configuration 2 had a superior performance to configuration 1.

To further evaluate the permeability quality of PVDF(M)/PVA hybrid membrane, a Lithium foil mass pick-up technique has been developed. Similar to Method 2 as described in 3.2.3.2, in the mass pick-up method, the Lithium foil is also sealed inside the bag. Rather than observing the visual changes but monitoring the mass change of the bagged Li ribbon that is exposed to air or in moisture chamber. With the new method developed here, one can quantitatively study the permeability property of the polymer membranes. To implement the mass pick-up method, the initial mass of Lithium foil before bagging as well as after bagging (Li foil+ membrane bag) are measured first inside the glove box. Upon exposure the bagged Lithium foil to an ambient environment, its mass is constantly monitored/recorded at a specified time interval for a total duration of 72 hours to study air and water moisture permeation issues. The mass pick-up is a
result of Li oxidation by air and water moisture permeating through the hybrid membrane when they are exposed either to air or moisture-controlled environment. The above concept can be expressed mathematically as:

\[
M_{\text{total}}(t) = M_{\text{total}}(t=0) + M_{\text{H}_2\text{O}}
\]

\[
M_{\text{H}_2\text{O}} = M_{\text{total}}(t) - M_{\text{total}}(t=0)
\]

**Relative Mass Take Up %** \[ = \frac{M_{\text{H}_2\text{O}}}{M_{\text{Li}(t=0)}} \]  \[
3.3
\]

where \( M_{\text{Li}}(t=0) \) is the initial mass of Lithium foil in glove box at time \( t=0 \); \( M_{\text{total}}(t=0) \) is the initial mass of Li + celgar separator+ PVDF/PVDF hybrid membrane in glove box; and \( M_{\text{total}}(t) \) is the mass of oxidized Li + celgar separator+ PVDF/PVDF hybrid membrane after exposing to ambient environment for time duration of \( t \).

With plotting **Relative mass take up %** versus **time t**.

\[
d\left[\frac{M_{\text{H}_2\text{O}}}{M_{\text{Li}(t=0)}}\right]
\]

One can examine the slope, \( \frac{d}{dt} \left[\frac{M_{\text{H}_2\text{O}}}{M_{\text{Li}(t=0)}}\right] \) to evaluate the time-dependent mass pick up rate.

This is a quantitative indicator to characterize the permeation rate of water/air through the hybrid membrane. In the mass pick-up experiments being performed in this study, two membrane bag configurations were used. One was PVDF(M) bag; and another is PVDF(M)/PVA bag with Celgar 3501 separator as the protection layer of Li ribbon. The bagged Li ribbon has been exposed to air as well as moisture chamber with humidity controlled at 50% and 100%.

**3.2.5 Electrochemical cell setup for evaluation of the EIS behavior and ionic conductivity of PVA/PVDF hybrid membranes**

Electrochemical Impedance Spectroscopy (EIS) was performed to investigate the ionic conductivity of PVA/PVDF hybrid membranes. Impedance spectroscopy is a favored technique for this purpose, as it can clearly separate the electrode response from the electrolyte, separator, PVA/PVDF hybrid membrane resistances. A typical AC impedance spectrum is given by a semicircle when the real part of the impedance at different frequencies is plotted against the
corresponding imaginary part values. The intercept of the semicircle with the real axis at high frequency corresponds to the ohmic resistance of the cell, which is dominated by the bulk resistances of the electrolytes, PVA/PVDF hybrid polymer membrane. The diameter of the semicircle is a reflection of interfacial impedances. An equivalent circuit is typically useful for mimicking the electrochemical response of the testing cell to assist the EIS data interpretation and ionic conductivity evaluation.

3.2.5.1 Electrochemical Test Cell Assembly
An electrochemical cell with PVA/PVDF(M) hybrid electrolytes was set up to investigate the EIS behaviors and measure the ionic conductivity of the prepared PVA/PVDF(M) hybrid membranes. Figure 3.2.5.2 schematically shows the test cell. The anodic and cathodic materials employed for the testing cell are Lithium and Nickel foils respectively. To prepare the anode, a piece of Lithium metal foil was enclosed and sealed with organic electrolyte (1M solution of LiPF$_6$ in THF/PC) in the PVA/PVDF(M) (60µm) membrane pouch. It is noted that, in the assembly of the anode, the hydrophobic PVDF side of the hybrid membranes should be the interior wall of the bag and in contact with the organic electrolyte while the hydrophilic PVA side film should be the exterior wall of the bag. In addition, a thin copper foil was also included as the current collector. This copper foil was electroplated with a piece of copper mesh, which is in contact with the Li foil by gently pressing. To prevent the direct contact between Li foil and PVA/PVDF membrane, a monolayer of Celgard 3501 separator (from Celgard) of 20µm thickness was used to separate Li foil from the interior wall of the bag (Figure 3.2.5.2.6). The anode was assembled in Argon filled Glove box and eventually sealed by Sili-Thane 803 (an Elastomeric sealant/adhesive) and left to set for one day before its use in the testing cell. Before performing the EIS test, the testing cell was completed by immersing the anode assembly in the aqueous electrolyte (diluted LiOH or diluted Acetic acid), in which the Nickel foil cathode is also immersed. In addition to the bagged assembly, the electrochemical cell, which consists of lithium foil| Celgar 3501 separator,1M solution of LiPF6 (Lithium Hexaflourophosphite) in tetrahydrofuran (THF)/propylene carbonate (PC) ) organic electrolyte, PVA/PVDF hybrid membrane, 1M solution of LiOH aqueous electrolyte|Nickel foil (Figure 3.2.5.2.6), was also applied for EIS experiment. In this cell, the working electrode – Lithium and counter electrode - Nickel was separated at distance of 10.09mm. It should be noted that, in the assembly of this test
cell, the hybrid electrolytes were separated by PVDF/PVA hybrid membrane with the hydrophobic PVDF facing the organic electrolyte and the hydrophilic PVA in contact with the aqueous electrolyte.

### 3.2.5.2 Electrochemical Impedance and Ionic conductivity measurements

The Electrochemical Impedance spectroscopy (EIS) measurements of the Electrochemical cell were carried out using Gamry Instruments Reference 3000. The aim here is to obtain the ionic conductivity of the PVA/PVDF hybrid membrane. Two-electrode and four-electrode configuration were used for the EIS experimental investigations. EIS measurements were done in potentiostatic mode. In the potentiostatic mode, a superposition of a fixed DC potential and a sinusoidal potential perturbation are applied to the test cell. With measuring the resultant current, the impedance characteristics of the system being tested can be determined. In the impedance measurement being performed in this thesis work, a 5mV sinusoidal stimulus over a defined frequency range (1MHz to 0.1Hz) has been applied. The impedance results are typically interpreted with a Nyquist plot – a plot of the Real ($Z'$) versus Imaginary ($Z''$) parts of the impedance at various frequency. The real $Z'$-axis intercept corresponds to the ohmic resistance of the Electrochemical cell, which is dominated by the bulk resistance contributed by PVA/PVDF hybrid polymer, electrolytes used and the separator. The equivalent circuit of the testing cell used for evaluating the ionic conductivity of the hybrid membranes is shown in Figure 3.2.5.2.1. Clearly, the bulk resistance of the electrochemical cell under investigation is made up of individual resistance contributions from the PVDF/PVA hybrid membrane, the Celgar 3501 separator, organic electrolyte and aqueous electrolytes. Mathematically, we have:

\[
R_a = \sum_{i=1}^{N} R_i
\]

Where, $R_a$ is the bulk resistance of the cell and $R_i$ is the individual ohmic resistances contributed by Celgar separator + organic electrolyte, aqueous electrolyte and PVA/PVDF(M) hybrid membrane.

To single out the resistance of the PVA/PVDF(M) hybrid membrane, the individual ohmic resistance of the Celgar 3501 separator, organic electrolyte, and the aqueous electrolyte has to be
subtracted from the bulk resistance of the test cell. For this purpose, three separate EIS experiments were performed. One is for the cell without PVA/PVDF(M) hybrid membrane but with only Celgar separator, organic electrolyte (figure 3.2.5.2.5), another is for only aqueous electrolytes (Figure 3.2.5.2.4); and for the complete cell (Figure 3.2.5.2.3). With the computed value of $R_s$ – the bulk resistance of the PVA/PVDF hybrid membrane, the ionic conductivity can be accordingly determined by:

$$\sigma = \frac{l}{R_sS}$$

Where, $l$ is the membrane thickness, and $S$ is the exposed cross-sectional area of the membrane sample.

Figure 3.2.5.2.1: Equivalent circuit model of the Electrochemical Test cell Assembly for High frequency spectra.

Figure 3.2.5.2.2: Fabrication of Anode assembly (A) Copper foil (current collector) electroplated with Copper Mesh. (B) Anode Pouch - Copper foil glued together with PVA/PVDF hybrid membrane bag.
Figure 3.2.5.2.3: Picture showing: Experiment 1 – Testing cell to scan EIS spectra for Li anode + Celgar separator//organic electrolyte//PVAIPVDF hybrid membrane//aqueous

Figure 3.2.5.2.4: Picture showing: Experiment 2 – Testing cell to scan EIS spectra for Nickel anode //organic //aqueous electrolyte//Nickel cathode Cell
Figure 3.2.5.2.5: Picture showing: Experiment 2 – Testing cell to scan EIS spectra for Nickel anode //organic //aqueous electrolyte//Nickel cathode Cell

Figure 3.2.5.2.6: Schematic diagram of Electrochemical Testing cell set up - Li anode + Celgar separator//organic electrolyte//PVA|PVDF hybrid membrane//aqueous electrolyte//Nickel cathode Cell
CHAPTER FOUR

RESULT AND DISCUSSION

4.1 Effects of processing conditions on membrane structure

The processing conditions were varied to investigate their effects on the surface morphology of solution cast PVA/PVDF hybrid membranes. It was observed that, among different processing conditions in the membrane preparation, the temperature set to evaporate the solvent has the most profound effect on the membrane surface morphology. With varying the solvent evaporation temperature at 60°C and 100°C for PVDF solution and 80°C and 120°C for PVA solution, the PVA/PVDF hybrid membranes were prepared. Figure 4.1.1 shows the surface morphology examined by SEM for such formed PVA/PVDF hybrid membranes. Clearly, with increasing the solvent evaporation temperature, the pore size for PVDF increased accordingly. However, for PVA, there was no such a trend observed.

(b) SEM image of PVA side of Batch 2 hybrid PVA/PVDF membrane (Solvent evaporation temperature =100°C)
(b) SEM image of PVA side of Batch 2 hybrid PVA/PVDF membrane (Solvent evaporation temperature =120°C)

(b) SEM image of PVDF side of Batch 2 hybrid PVA/PVDF membrane (Solvent evaporation temperature =60°C)
Figure 4.1.1: SEM Images of Solution processed PVA and PVDF membranes

4.2 Stability of solution processed hybrid Membranes

According to the procedures described in Ch. 3, the stability of the PVA/PVDF hybrid membrane in organic and aqueous electrolytes was tested. The visual observation results are shown in Figure 4.2.1.1. The PVDF and PVA films showed no visual changes after immersion in organic electrolyte (1M solution of tetrahydrofuran (THF)/propylene carbonate (PC) and LiPF6 (Lithium Hexafluorophosphate) for 3 days. This shows that both polymer films are stable in the organic electrolyte. Stability of the PVA/PVDF hybrid membrane in organic electrolyte suggests that as a Li-ion conducting membrane it will improve the performance of Li-Air battery air operated by dual electrolytes.
4.2.1 Stability result of PVA and PVDF films in Organic Electrolyte

(a) Sample of PVA and PVDF films before Immersion

(b) Samples of PVDF and PVA films immersed in organic electrolyte

(a) Samples of PVA and PVDF after immersion for 3 days in organic electrolyte indicated no visual changes

Figure 4.2.1.1: Stability Test via Visual Changes of of PVA and PVDF samples in Organic electrolyte (1M solution of LiPF$_6$ in THF/PC).
4.2.2 Stability of Solution processed PVA and PVDF in aqueous electrolyte

With the procedures described in Ch. 3, the stability of the solution processed PVA/PVDF hybrid membrane in aqueous electrolytes was also tested. The test was done for two different aqueous electrolytes, 1M LiOH solution in water and 1M acetic acid aqueous solution. Visual observation results are shown in Figure 19. The PVDF and PVA films showed no visual change after immersion in acetic acid aqueous electrolyte for 3 days. However, a visual change occurred when the solution processed PVA/PVDF hybrid membrane was immersed in LiOH aqueous electrolyte. The results obtained here indicate that the solution processed PVA/PVDF hybrid membrane was unstable in LiOH aqueous electrolyte but was stable in acetic acid aqueous electrolyte. The reasons for instability of the PVA/PVDF hybrid membrane in organic electrolyte is probably due to traces of NMP solvent that may complex with LiOH aqueous electrolyte to cause the film color change. To ascertain this assumption, the commercial PVDF(M), which does not contain any solvents, was also subjected to immersion test in LiOH aqueous electrolyte. The results are shown in Figure 4.2.2.1. In contrast to solution processed PVDF films, the melt extruded PVDF(M) films showed no visual change after 3 days when immersed in LiOH aqueous electrolyte (1M aqueous solution of LiOH). The comparison on the stability testing of PVDF(M) and solution processed PVA/PVDF hybrid membrane justifies that, in terms of immersion stability, both polymers can be used as Li ion conducting membrane for Li-air battery set up operated by dual electrolytes.

![Image](image-url)

Figure 4.2.2.1: Stability Test for solution processed PVA/PVDF hybrid in aqueous electrolyte

(A) PVA and PVDF solution showed visual changes after 3 days. (B) PVA and PVDF showed no visual changes after 3 days
Figure 4.2.2.2: Stability Test of melt extruded commercially available PVDF(M) film in LiOH aqueous electrolyte by observing Visual changes of films.
4.3 Permeability of solution processed PVA/PVDF hybrid membrane

4.3.1 Water permeation test by UV-VIS spectroscopy (Method - 1)

Figure 20 shows the results of water permeability test according to Method 1 - UV-VIS spectroscopy based technique as discussed in Ch. 3. As shown in Fig 4.3.1.1, it can be observed that the spectra of the samples of organic electrolyte taken from PVA/PVDF and polyethylene bags, which have been exposed to air and immersed in distilled water for permeation test, were similar to that of neat organic electrolyte. For these electrolyte samples, there is no peak feature at 2000 nm being observed. According to the spectra of the baseline samples - organic electrolyte with inclusion of various weight percent of distilled water, it is known that the peak at 2000 nm is due to water absorption. The lack of 2000 nm peaks in the organic electrolytes bagged in the PVA/PVDF and polyethylene bags that were subjected to immersion test in water shows that the solution processed PVA/PVDF hybrid membranes prepared in this study has a reasonable resistance to water permeation. Nevertheless the water permeation test result given by Method-1 is not directly relevant to the practical application of hybrid membranes in Li battery setup. Thus, this spectroscopy-based method was not considered an effective way for experimentally testing the water permeability for the hybrid membranes.
4.3.2 Using the visual changes technique to test water permeability for solution processed PVA/PVDF hybrid membranes

According to the test procedure discussed in Ch. 3 (Method-2), visual test technique was applied for testing the water permeability of the solution processed PVA/PVDF hybrid membranes. Figure 4.3.1.1 shows the results. The pictures in Figure 4.3.1.1 shows a visible surface change for the Lithium foil in the hybrid membrane bag after one hour immersion in water. This clearly indicates that the Lithium foil in the hybrid membrane bag was oxidized by water permeating through the membrane bag. This means that the porosity of the membrane was not adequate to prevent water molecules from permeating through the hybrid membrane. This result reveals that
the solution processed hybrid membrane in terms of water permeability is not satisfactorily suitable to improve performance for Li-Air battery setup operated by dual electrolytes.

Figure 4.3.2.1: Images (A), (B), (C) showing Li foil and organic electrolyte sealed in Solution processed PVA/PVDF hybrid membrane to demonstrate Water permeability by observing visual changes in Li foil
4.4 Melt and Solution processed hybrid membrane.

4.4.1 Permeability of melt and solution processed hybrid membrane by Visual Technique

4.4.1.1 Permeability by Visual Technique using melt extruded PVDF membrane bag

According to the procedures discussed in Ch. 3, the water permeability test was carried out for melt extruded PVDF(M) film bags. Figure 4.4.1.1.1 shows the results. Upon immersion in water, it took about 2 hours to observe the barely visible changes for the Li-foil bagged in PVDF(M) membranes. It took 1 day for the Li foil to be completely oxidized by water permeating through the PVDF(M) film. The rate at which the Li foil was oxidized appeared similar to both neat Li foil in PVDF(M) bag and Li foil with organic electrolyte in PVDF(M) bags. In comparison to solution based PVA/PVDF hybrid membrane, the melt extruded PVDF(M) film showed an improvement with regards to resistance to water permeation. This clearly indicates the melt extruded PVDF(M) film will offers an improved performance to Li-air battery in terms of water permeability than the solution processed PVA/PVDF hybrid membrane.

(A) Li foil in melt and solution processed PVDF membrane bag immersed in water, 10 minutes after taken out of Glove box
(B) Li foil in melt and processed PVDF Membrane bag immersed in water AFTER 1 HOUR

Li foils starts to oxidize

(D) Li foil in PVDF(M) film bag immersed in water AFTER 1 day

Li in organic oxidize Completely oxidized

Li in PVDF(M) bag oxidize Completely oxidized

(C) Li foil in melt PVDF(M) membrane bag immersed in water AFTER 2 HOURS

Li in organic starts to oxidize

Figure 4.4.1.1.1: Images (A), (B), (C) showing Visual Technique results of Lithium foil in Melt and Solution processed membrane bag immersed in distilled Water
4.4.1.2 Permeability test using solution based PVA/melt extruded PVDF hybrid membrane configurations

With the commercial PVDF(M) film as the substrate, PVA/PVDF(M) hybrid membranes were fabricated and tested for water permeation according to the procedures described in Ch 3. Figure 4.4.1.2.1 shows the results. In comparison to neat PVDF(M) membranes, the PVA/PVDF(M) hybrid membranes offer better water permeation resistance. It was also observed that the water permeation resistance for the PVA/PVDF(M) hybrid membrane bag can be enhanced, when the inner wall of the bag is made of PVDF(M) instead of PVA. In summary, the bag configuration for the PVA/PVDF(M) hybrid membrane bag is important in improving the water permeation performance suitable for Li-air battery set up operated with dual electrolytes.

(A) Lithium foil in PVDF(M)/PVA hybrid membrane bag configurations AFTER 30 minutes from glove box
Lithium foil in melt PVDF(M) in/solution PVA out hybrid membrane bag in water shows slower oxidation

Lithium foil in solution PVA in/PVDF(M) out hybrid membrane bag in water shows faster oxidation

(A) Lithium foil in PVDF(M)/solution processed PVA hybrid membrane bag configurations immersed in water AFTER 2 hours

Lithium foil in PVDF(M) out/solution PVA in hybrid membrane bag in water more oxidized

Lithium foil in solution PVA out/melt PVDF(M) in hybrid membrane bag in water shows slower oxidation

(C) Lithium foil in PVDF(M)/PVA hybrid membrane bag configurations immersed in water AFTER 6 hours

Figure 4.4.1.2.1: Images (A), (B), (C) showing Visual Technique results for Lithium in PVA in/PVDF(M) out and PVA out/ PVDF(M) in configurations membrane bag immersed in distilled water
4.4.2 Permeability Test using the Li foil mass pick up technique

According to the procedures described in Ch. 3, mass pick up experiments were performed for bagged Lithium foil. Table 4.4.2 shows the Lithium foil mass pick up results for the melt extruded PVDF (M) bag when exposed to air. Figure 4.4.2.1 shows the corresponding, mass gain percentage as a function of exposure time. According to the slope change, it was observed that, the Lithium foil mass pick-up rate was relatively slow when the exposure time is less than ~ 100mins. When the exposure time is longer than ~ 100 min, the mass pick-up rate increased rapidly. The results shown in Table 4.4.2 and Figure 4.4.2.1 clearly indicate that water/air permeation through the PVDF film is slower during the first 100mins and rapidly increases after 100 mins. The mass pick-up experiments seem to have a good agreement with the visual testing results which showed that a visual change on the Li foil surface occurred after immersion in water for 2 hours.

Li mass pick-up experiments were also performed for Li foils bagged in PVDF(M) and PVA/PVDF(M) hybrid membranes that were exposed to an moisture environment with humidity controlled at 50% and 100%. The results are respectively shown in Table 4.4.3 and Table 4.4.4. With the mass pick-up data listed in Table Table 4.4.3 and Table 4.4.4, Figure 4.4.2.2 and Figure 4.4.2.3 also show the corresponding log-log plot for the mass gain percentage as a function of exposure time. The results shown in Figure 4.4.2.2 and Figure 4.4.2.3 indicated that the mass pick up rate has been significantly reduced for the PVA/PVDF(M) hybrid membranes when compared to neat PVDF(M) films. This result is also consistent with the visual testing results discussed previously.

In summary, the mass pick-up experiment developed in this study is able to provide a quantitative test on the water/air permeation performance of various polymer membranes. In particular, the testing results indicates that the water permeability has been improved with the use of melt extruded PVDF/solution processed PVA hybrid membrane.
Table 4.4.2 Mass Pick up of Lithium foil in PVDF bag exposed to air

<table>
<thead>
<tr>
<th>Comments</th>
<th>Time (min)</th>
<th>Time (hr)</th>
<th>Mass (mg)</th>
<th>Li - mass gain (mg)</th>
<th>% mass gain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li ribbon in GB</td>
<td>0</td>
<td>0.00</td>
<td>40.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in GB</td>
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<td>0.00</td>
<td>87.12</td>
<td></td>
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</tr>
<tr>
<td>Li ribbon+PVDF Bag in Air</td>
<td>10</td>
<td>0.17</td>
<td>87.27</td>
<td>0.15</td>
<td>0.003749063</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Air</td>
<td>15</td>
<td>0.25</td>
<td>87.27</td>
<td>0.15</td>
<td>0.003749063</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Air</td>
<td>20</td>
<td>0.35</td>
<td>87.32</td>
<td>0.2</td>
<td>0.00499875</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Air</td>
<td>25</td>
<td>0.42</td>
<td>87.34</td>
<td>0.22</td>
<td>0.005498625</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Air</td>
<td>30</td>
<td>0.50</td>
<td>87.35</td>
<td>0.23</td>
<td>0.005748569</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Air</td>
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<td>0.58</td>
<td>87.36</td>
<td>0.24</td>
<td>0.00599885</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Air</td>
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<td>0.67</td>
<td>87.37</td>
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<td>0.006248438</td>
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<tr>
<td>Li ribbon+PVDF Bag in Air</td>
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<td>87.39</td>
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<td>0.006748313</td>
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<td>0.83</td>
<td>87.41</td>
<td>0.29</td>
<td>0.007248188</td>
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<tr>
<td>Li ribbon+PVDF Bag in Air</td>
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<td>0.92</td>
<td>87.42</td>
<td>0.3</td>
<td>0.007998</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Air</td>
<td>60</td>
<td>1.00</td>
<td>87.44</td>
<td>0.32</td>
<td>0.007998</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Air</td>
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<td>1.00</td>
<td>87.44</td>
<td>0.32</td>
<td>0.007998</td>
</tr>
<tr>
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<td>87.61</td>
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<td>87.86</td>
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<td>1.3</td>
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<td>1.71</td>
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</tr>
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<td>89.18</td>
<td>2.06</td>
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<td>89.58</td>
<td>2.46</td>
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<tr>
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<td>15.00</td>
<td>92.32</td>
<td>5.7</td>
<td>0.142464384</td>
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<tr>
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<td>23.00</td>
<td>94.56</td>
<td>7.44</td>
<td>0.18953512</td>
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<tr>
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<td>31.00</td>
<td>97.02</td>
<td>9.9</td>
<td>0.24749814</td>
</tr>
<tr>
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<td>2340</td>
<td>39.00</td>
<td>100.5</td>
<td>17.98</td>
<td>0.449878653</td>
</tr>
<tr>
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<td>47.00</td>
<td>109.48</td>
<td>22.36</td>
<td>0.558860285</td>
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<tr>
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<td>55.00</td>
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<tr>
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<td>117</td>
<td>29.88</td>
<td>0.746813297</td>
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<tr>
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<td>4260</td>
<td>71.00</td>
<td>121.56</td>
<td>34.44</td>
<td>0.860784804</td>
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Figure 4.4.2.1: Graph Showing mass pick up as a function of time of Lithium foil sealed in melt extruded PVDF membrane bag exposed to air
Table 4.4.3 Relative Mass Take up of Lithium foil in PVDF(M) and hybrid membrane bag in moisture chamber 50%

<table>
<thead>
<tr>
<th>Comments (in 58% moisture chamber)</th>
<th>Time (min)</th>
<th>Time [hr]</th>
<th>Mass [mg] PVDF only</th>
<th>Hybrid mass PVDF-in/PVA-out</th>
<th>Relative mass take-up % PVDF only</th>
<th>Relative mass take-up % PVDF-in/PVA-out</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li ribbon in GB</td>
<td>0</td>
<td>0.00</td>
<td>31.1</td>
<td>31.8</td>
<td>0.98 (0)</td>
<td>0.98 (0)</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in GB</td>
<td>10</td>
<td>0.17</td>
<td>48.7</td>
<td>167.7</td>
<td>0.0061 (1508)</td>
<td>0.0039 (0664)</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
<td>15</td>
<td>0.25</td>
<td>99.1</td>
<td>168.1</td>
<td>0.0019 (968)</td>
<td>0.0069 (444)</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
<td>20</td>
<td>0.33</td>
<td>99.4</td>
<td>168.9</td>
<td>0.0325 (8784)</td>
<td>0.0071 (8529)</td>
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<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
<td>25</td>
<td>0.42</td>
<td>99.6</td>
<td>168.4</td>
<td>0.0051 (2957)</td>
<td>0.0071 (2973)</td>
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<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
<td>30</td>
<td>0.50</td>
<td>99.7</td>
<td>168.7</td>
<td>0.0060 (9086)</td>
<td>0.0095 (0105)</td>
</tr>
<tr>
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<td>55</td>
<td>0.73</td>
<td>99.9</td>
<td>168.9</td>
<td>0.0187 (40614)</td>
<td>0.0207 (1193)</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
<td>50</td>
<td>0.83</td>
<td>100</td>
<td>169</td>
<td>0.0195 (8732)</td>
<td>0.0137 (9457)</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
<td>55</td>
<td>0.94</td>
<td>100.1</td>
<td>169.1</td>
<td>0.0230 (8732)</td>
<td>0.0137 (9861)</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
<td>60</td>
<td>1.00</td>
<td>100.2</td>
<td>169.1</td>
<td>0.0134 (6728)</td>
<td>0.0137 (9861)</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
<td>55</td>
<td>1.30</td>
<td>100.4</td>
<td>169.3</td>
<td>0.0204 (4944)</td>
<td>0.0134 (6257)</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
<td>100</td>
<td>2.00</td>
<td>100.5</td>
<td>170.3</td>
<td>0.0244 (9832)</td>
<td>0.0134 (6209)</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
<td>120</td>
<td>2.50</td>
<td>100.8</td>
<td>170.5</td>
<td>0.0272 (2936)</td>
<td>0.0134 (6703)</td>
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<td>Li ribbon+PVDF Bag in Moisture</td>
<td>130</td>
<td>3.00</td>
<td>101</td>
<td>171.1</td>
<td>0.0293 (1672)</td>
<td>0.0134 (6703)</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
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<td>4.00</td>
<td>101.4</td>
<td>171.8</td>
<td>0.0330 (3914)</td>
<td>0.0282 (087)</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
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<td>5.00</td>
<td>101.8</td>
<td>172.8</td>
<td>0.0371 (1631)</td>
<td>0.0345 (1311)</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
<td>350</td>
<td>6.00</td>
<td>102.3</td>
<td>173.8</td>
<td>0.0428 (1496)</td>
<td>0.0400 (7751)</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
<td>440</td>
<td>7.00</td>
<td>102.7</td>
<td>175.4</td>
<td>0.0466 (5923)</td>
<td>0.0460 (7995)</td>
</tr>
<tr>
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<td>450</td>
<td>7.50</td>
<td>102.9</td>
<td>176.9</td>
<td>0.0507 (7517)</td>
<td>0.0482 (6063)</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
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<td>15.00</td>
<td>105.2</td>
<td>178.6</td>
<td>0.0723 (7517)</td>
<td>0.0668 (4063)</td>
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<td>1300</td>
<td>23.00</td>
<td>109.9</td>
<td>181.5</td>
<td>0.1302 (8435)</td>
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<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
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<td>31.00</td>
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<td>183.9</td>
<td>0.1471 (8991)</td>
<td>0.0818 (6823)</td>
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<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
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<td>115.3</td>
<td>184.9</td>
<td>0.1753 (2125)</td>
<td>0.0862 (304)</td>
</tr>
<tr>
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<td>47.00</td>
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<td>130.5</td>
<td>187.7</td>
<td>0.2202 (1843)</td>
<td>0.1368 (8039)</td>
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<td>63.00</td>
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<td>188.5</td>
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<td>189.9</td>
<td>0.2772 (6894)</td>
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Figure 4.4.2.2: Log-log plot for the mass gain percentage as a function of exposure time of extruded PVDF and solution processed PVA Hybrid membrane bag in 50% moisture chamber.
Table 4.4.4 Relative Mass Pick up rates of Lithium foil in PVDF and hybrid membrane bag in Moisture Chamber 100%

<table>
<thead>
<tr>
<th>Comments (moisture)</th>
<th>Time (min)</th>
<th>Time (hr)</th>
<th>Massing/Moisture chamber (PVDF)</th>
<th>Massing/Moisture chamber (hybrid)</th>
<th>Massing/Moisture chamber (PVDF out)</th>
<th>Massing/Moisture chamber (PVDF in)</th>
<th>Massing/Moisture chamber (PVDF out)</th>
</tr>
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<td>Li ribbon in 6S</td>
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<td>0.00</td>
<td>0.00</td>
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<td>Li ribbon+PVDF Bag in 6S</td>
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<td>0.00</td>
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<td>0.00</td>
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<td>0.39</td>
<td>0.00</td>
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<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
<td>20</td>
<td>0.50</td>
<td>0.00</td>
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<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
<td>20</td>
<td>0.50</td>
<td>0.00</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Li ribbon+PVDF Bag in Moisture</td>
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<td>0.50</td>
<td>0.00</td>
<td>0.00</td>
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4.5 Electrochemical Impedance Spectroscopy Measurements

According to the procedures discussed in Ch. 3, the EIS experiments were performed on PVA/PVDF hybrid membranes. Figure 4.51, 4.5.2, 4.5.3 show the Nyquist plot respectively for a complete test cell (Li//Celgard separator + organic electrolyte/PVA_PVDF-Hybrid membrane/aqueous electrolyte//Nickel foil ), a cell without hybrid membrane in aqueous electrolyte (Nickel// 1M solution of LiOH (aqueous electrolyte)//Nickel ), and a cell without hybrid membrane in organic electrolyte (Ni//Celgar 3501 separator in organic electrolyte//Ni).
Figure 4.5.1: Typical Nyquist plot for Li// Celgard separator+organic electrolyte/PVA_PVDF-Hybrid membrane/aqueous electrolyte//Nickel foil Cell

Ohmic resistance = 8.45Ω
Figure 4.5.2: (A) Typical Nyquist plot for Nickel// 1M solution of LiOH (aqueous electrolyte)//Nickel Cell (B) Schematic diagram of Nickel// 1M solution of LiOH (aqueous electrolyte)//Nickel Cell

Ohmic resistance = 1.85Ω

Working electrode area = 14mm x 14mm

Nickel electrodes

1M solution of LiOH aqueous electrolyte
Figure 4.5.3: (A) Typical Nyquist plot for Celgar 3501 separator in 1M solution of THF/PC and LiPF$_6$ with Nickel electrodes. (B) Schematic diagram of Ni//celgar 3501 separator in organic electrolyte//Ni cell
With the results shown in Figure 4.5.1, 4.5.2, and 4.5.3, the ionic conductivity of the PVA/PVDF hybrid membranes can be computed as following.

According to Figure 4.5.1, the ohmic resistance for the complete cell (Li electrode + Celgard separator//organic electrolyte// (PVA/PVDF)hybrid electrolyte// Nickel electrode, cell geometry parameter: \( S=1.96\text{cm}^2 \) and \( l=1.009\text{cm} \)) was determined by the intercept on the real impedance axis, which is:

\[
Ra = 8.45\Omega
\]

Similarly, the ohmic resistance for Nickel//aqueous electrolyte//Nickel cell (cell geometry parameter: \( S=1.96\text{cm}^2 \) and \( l=1.009\text{cm} \)) can also be determined respectively according to Figure 4.5.2, and 4.5.3 as:

\[
R_{aq} = 1.85 \Omega
\]

and

\[
R_{sep+org} = 1.404 \Omega
\]

With correcting the cell geometry parameter in obtaining \( R_{sep+org} \) (\( S=1.13\text{cm}^2 \) and \( l=1\text{cm} \)) to match the one for measuring \( Ra \) and \( R_{aq} \) (\( S=1.96\text{cm}^2 \) and \( l=1.009\text{cm} \)), the corrected \( R_{(sep+org)} \) was determined as:

\[
R_{(sep+org)} = 0.829 \Omega
\]

With neglecting the interfacial resistances between the hybrid membrane and the electrolytes, the resistance of the PVA/PVDF hybrid membrane can then be computed as:

\[
R_{(hyb-mem)} = Ra - R_{(sep+org)} \cdot R_{aq}
\]

\[
= 8.45-(0.829+1.85) \Omega
\]

\[
= 5.771 \Omega
\]

According to the membrane dimension (thickness \( \times \) area = \( 6\times10^{-3}\text{cm} \times 1.96\text{cm}^2 \)), then the Ionic conductivity of the PVA/PVDF hybrid membrane can be calculated from the expression with equation 3.5 in Ch. 3 as:

\[
\sigma = 5.3\times10^{-4}\text{Scm}^{-1}
\]

This result is satisfactory for Li-air battery application.
CHAPTER FIVE

CONCLUSION AND FUTURE WORK

5.1 Conclusion

The present thesis work focused on developing solution processed PVA/PVDF hybrid membranes and examining the relevant key physical characteristics, e.g., water permeation and ionic conductivity, for their potential use in Li-air batteries. In the developed hybrid membrane, the hydrophobic PVDF offers the barrier to prevent water permeation and thus is able to protect the Li anode from being oxidized. The hydrophilic PVA provides mechanical support and enhances the ionic conductivity of the hybrid membrane. With the sequential solution deposition – solvent evaporation processing method developed in this study, PVA/PVDF hybrid membranes have been successfully developed. The hybrid membranes prepared at different processing conditions have been proved to be stable to both aqueous and organic electrolytes. In terms of water permeation property, the solution processed PVA/PVDF hybrid membranes are inferior to the commercially available neat PVDF films. This is attributed to the pore structure formation in the solution processed PVA/PVDF hybrid membranes, which could be mitigated by using low solvent evaporation temperature as demonstrated in this study. The electrochemical impedance spectroscopy (EIS) has been applied to evaluate the ionic conductivity of PVA/PVDF membranes. The EIS measurements indicate that the ionic conductivity of the PVA/PVDF was satisfactory. In conclusion, the research work presented in this study tested the feasibility of using hydrophilic PVA/hydrophobic PVDF hybrid membrane to improve the performance of lithium air battery operated by a dual electrolyte (organic and aqueous electrolytes) configuration.
5.2 Future Work

This research can be further improved upon in several ways. First is to carry out some more investigations on water permeability by analysis of the pore structures of melt and solution processed PVA/PVDF hybrid films. Another is to try cross-linking the PVA and PVDF polymer matrix to further enhance their thermal and electrolyte-immersion stability. With this approach, the water permeability and ionic conductivity of the PVA/PVDF hybrid membranes can also be fine-tuned.
REFERENCES


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BIOGRAPHICAL SKETCH

Emem Akpanekong is from Akwa Ibom, Nigeria. He graduated with Honors from the Federal University of Technology, Owerri, Nigeria with a Bachelor of Engineering in Electrical and Electronics Engineering in August 2006. In the summer of 2012, he will graduate with Master of Science in Electrical Engineering.